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XV.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

By C. Loring Jackson.

THIRD PAPER.

ON PARAIODBENZYL COMPOUNDS.

C. F. Mabery.

Presented May 9, 1877.

The preparation of *paraiodbenzylbromide*, $C_6H_4ICH_2Br$, has been described in the first article of this series;* but the method there given did not invariably yield good results, the product often being mixed with a black tar which it was very hard to remove completely by crystallization. A more careful study of the conditions of the reaction has shown that this was due to an oily impurity of the iodtoluol, a very small amount of which was sufficient to destroy a great part or even the whole of the paraiodbenzylbromide: if the paraiodtoluol purified by distillation was carefully pressed between filter-paper, this oil was absorbed, and then the product of the bromiring was nearly white after the first crystallization. When the purified paraiodtoluol was used, the yield was very nearly the same, averaging 4.7 grs. of pure bromide from 10 grs. of iodtoluol, when the bromiring took place at 115°, 130°, or 150° (one-half of the thermometer-bulb dipping in the liquid), while at temperatures below 115° the bromiring was slow, and the amount of paraiodbenzylbromide formed small. These observations are important, because they tend to fix, in the case of paraiodtoluol, the limit at which bromine ceases to enter the main ring in any great amount, and thus one step is taken toward giving a more definite form to Beilstein's rule about the action of bromine on toluol and its homologues.[*] At temperatures above 150°, I observed the liberation of iodine, but, as already stated in the first paper on this subject, paraiodbenzylbromide was formed, although according to Beilstein[†] bromine enters the ring even at the boiling-point of toluol, if iodine has been added. This exception to Beilstein's rule has suggested a series of experiments, which will be carried on in this laboratory, to determine what effect, if any, the nature and position of the radical attached to the main ring exercise upon the bromiring of substituted toluols.

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* These Proceedings, Vol. XII. (n. s. IV.) p. 219.

The following substances were obtained from paraiodbenzylbromide by the usual metathetical reactions: —

Paraiodbenzylalcohol, $C_6H_4ICH_2OH$, was prepared from the product of the action of sodic acetate on the bromide, by heating it to 160° with aqueous ammonia in a sealed tube: the solid thus obtained was purified by pressing between filter-paper, and crystallization from carbonic disulphide. It was also made[‡] by boiling paraiodbenzylbromide with water for several hours in a flask with a return-condenser: that hydrobromic acid was set free, was proved by the acid reaction of the water, and the precipitate of argentic bromide formed on adding argentic nitrate to it, after the organic matter had been removed.

The alcohol prepared according to the first method was analyzed.

0.2508 gr. substance gave 0.3260 gr. CO_2 and 0.0633 gr. H_2O.

	Calculated for C_7H_6IOH.	Found.
Carbon	35.89	35.45
Hydrogen	2.99	2.79

Properties. It crystallizes from carbonic disulphide or alcohol in small silky white scales; from boiling water, in long needles, with an aromatic odor like that of the corresponding bromine compound, but no action on the eyes; melting-point, 71¾°; very slightly soluble in cold, somewhat more soluble in hot water; freely in alcohol, ether, benzole, and carbonic disulphide.

The *paraiodbenzylacetate* was not obtained pure, because, on account of its instability, a great quantity of substance would have been consumed in its preparation; and it did not seem worth while to sacrifice the large amount of time necessary to prepare so much paraiodbenzylbromide, especially as its decompositions seemed analogous to those of the more accessible parabrombenzylacetate, which will be studied in this laboratory. The following account of the attempts to prepare it is, however, given, as it throws some light upon the nature of the substance. The first difficulty encountered was due to the fact that the sodic acetate only partially decomposed paraiodbenzylbromide. The two substances were boiled with absolute alcohol, and an oily product obtained, which solidified at 0°, and after crystallization from alcohol melted at 45°: the results of an analysis of this substance are given under I.; it was then heated once more with sodic acetate and absolute alcohol, and the result analyzed, when the numbers given under II. were obtained.

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[*] These numbers have been tested and confirmed in this laboratory by Mr. A. W. Field, who will publish his results in detail, as well as similar experiments upon other substituted toluols, in a later paper of this series. — [C. L. J.]

[†] Ann. Chem. Pharm. 143, p. 369.

[‡] These Proceedings, Vol. XII. (N. S. IV.) p. 221.

I. 0.4007 grs. substance gave 0.4416 gr. CO_2 and 0.0909 gr. H_2O.

II. 0.2936 gr. substance gave 0.3403 gr. CO_2 and 0.0738 gr. H_2O.

	Calculated $C_7H_6IC_2H_3O_2$.	Found. I.	Found. II.	Calculated C_7H_6IBr
Carbon	39.12	30.05	31.61	28.28
Hydrogen	3.26	2.52	2.79	2.03

These numbers seem to show that the substance was nothing more than a mixture of the acetate and bromide, and this conclusion is strengthened by the fact that it attacked the eyes like the bromide. In order to obtain the acetate from this mixture, it would have been necessary to use fractional distillation, which had been found, in the case of parabrombenzylacetate, to cause almost complete decomposition: it was therefore thought better to try to decompose the paraiodbenzylbromide completely by using argentic, instead of sodic, acetate. In this case, the product was an oil, which showed no signs of solidification, even after standing in an open watch-glass for some time. The term then came to an end, and it remained exposed to the air during the summer vacation of three months, at the end of which time the watch-glass contained a solid residue, proved to be paraiodbenzoic acid by its melting-point and the following analysis of its silver salt: —

0.2185 gr. substance gave by precipitation with hydrochloric acid 0.0857 gr. AgCl.

	Calculated for $C_6H_4ICO_2Ag$.	Found.
Silver	30.42	29.62

The formation of this acid under these conditions can be explained by the supposition that the acetate absorbed water from the atmosphere, and became converted into the alcohol, which was then oxidized by exposure to the action of the air; and this view is supported by the observation, that a product from the reaction of paraiodbenzylbromide on sodic acetate dissolved in ordinary alcohol, when precipitated by water, and the oil thus obtained allowed to stand exposed to the air in a watch-glass, deposited crystals, which upon recrystallization melted at 70°, and were, therefore, the alcohol. It must, however, be remembered that this oil contained some of the bromide, and that the alcohol may have been formed from this instead of the acetate. This conversion of the acetate into the alcohol or acid seemed likely to render its purification so difficult that the experiment with argentic acetate was not repeated. A similar formation of the substituted benzoic acid has been observed in the attempts to purify parabrombenzylacetate.

Paraiodbenzylcyanide, $C_6H_4ICH_2CN$, was obtained by boiling the bromide with alcoholic potassic cyanide, precipitating with water, and crystallizing from alcohol. Its composition was established by the following nitrogen determination: —

0.3523 gr. substance gave 17.83 cc. nitrogen, under a pressure of 736. mm. and a temperature of 23°.

	Calculated for C_7H_6ICN.	Found.
Nitrogen	5.76	5.67

Properties. White plates with a pearly lustre, characteristic odor, and no action on the eyes; melting-point, 50½°; insoluble in water; readily soluble in alcohol, ether, benzole, carbonic disulphide, and glacial acetic acid.

Paraiodalphatoluylic acid, $C_6H_4ICH_2COOH$, was obtained by heating the cyanide with fuming hydrochloric acid to 100° in a sealed tube: after four hours, the liquid on cooling became filled with flattened needles, which were purified by crystallization from boiling water. The composition of the acid was fixed by the analysis of its silver salt.

Properties. Narrow, tapering, white plates, often over two centimeters long, with an agreeable odor resembling that of sweet alyssum; melting-point, 135°, sublimes in branching needles at a somewhat higher temperature; but slightly soluble in cold, readily in hot water, and in alcohol, ether, benzole, carbonic disulphide, and glacial acetic acid. A mixture of potassic dichromate and dilute sulphuric acid oxidizes it, forming paraiodbenzoic acid, which was recognized by its high melting-point. It is freely soluble in aqueous ammonia, but the ammonium salt could not be obtained in the solid state, as evaporation of the solution, whether on the water-bath or *in vacuo*, at ordinary temperatures, decomposed it, leaving the acid, which was recognized by its sparing solubility in cold water and its melting-point of 135°.

Argentic paraiodalphatoluylate, $C_6H_4ICH_2COOAg$, was made by adding the solution of the acid in ammonia water, from which the excess of ammonia had been driven off by warming on the water-bath, to argentic nitrate: the white curdy precipitate was washed, dried *in vacuo*, and analyzed.

0.7065 gr. substance, dissolved in dilute nitric acid and precipitated with hydrochloric acid, gave 0.2701 gr. of argentic chloride.

0.1214 gr. substance gave 0.0475 gr. of argentic chloride.

	Calculated for $C_8H_6IO_2Ag$.	Found.	
		I.	II.
Silver	29.27	28.78	29.45

Properties. A white curdy precipitate resembling argentic chloride, sparingly soluble in boiling water, from which it crystallizes in lustrous plates; readily soluble in dilute nitric acid. The dry salt is only slightly blackened by heat and light.

Baric paraiodalphatoluylate, $Ba(C_6H_4ICH_2COO)_2 . H_2O$, prepared by neutralizing baric hydrate with a hot aqueous solution of the acid, and evaporating to crystallization, gave the following results on analysis: —

0.5400 gr. substance dried *in vacuo* lost, when heated to 100°, 0.0153 gr., and gave 0.1881 gr. $BaSO_4$.

	Calculated $Ba(C_8H_6IO_2)_2 . H_2O$.	Found.
Water	2.66	2.83
Barium	20.23	20.48

It forms microscopic white needles, easily soluble in water.

The *calcium salt*, made by treating calcic carbonate with a concentrated aqueous solution of the acid, was also freely soluble in water, and crystallized in slender branching needles.

The solution of the ammonium salt of the acid obtained by dissolving it in aqueous ammonia, and driving off the excess of ammonia on the water-bath, behaved as follows with various reagents: —

With *cupric sulphate*, pale bluish-green flocks, insoluble in water, but soluble in acids.

With *ferric chloride*, pale yellowish-brown flocks, insoluble in water.

With *chromic chloride* or *nickelous nitrate*, a green precipitate.

With *cobaltous nitrate*, a pink precipitate.

With *plumbic acetate*, *mercurous nitrate*, or *aluminic chloride*, a white flocculent precipitate.

With *zincic* and *manganous nitrate*, salts which are sparingly soluble in water and crystalline; the manganese salt is flesh-colored. No precipitate was obtained with salts of *cadmium*, *magnesium*, *strontium*, and the *alkaline metals*. In general, its salts resembled very closely those of the corresponding parabromalphatoluylic acid.

Paraiodbenzylsulphocyanate, $C_6H_4ICH_2SCN$, was made by boiling an alcoholic solution of potassic sulphocyanate with paraiodbenzylbromide: the oil obtained by precipitating the product with water solidified upon cooling, and was purified by draining on filter-paper, and crystallization from hot alcohol.

0.3661 gr. substance gave 0.4702 gr. CO_2: the water was lost by breaking the chloride of calcium tube.

0.2159 gr. substance gave, according to Carius, 0.1844 gr. baric sulphate.

	Calculated for C_7H_6ISCN.	Found.
Carbon	34.91	35.02
Sulphur	11.64	11.72

Properties. It crystallizes from alcohol in long white lustrous plates which are often twinned; it has a slight but disagreeable odor, like that of the benzylsulphocyanate; melting-point, 40¼°; insoluble in water; slightly soluble in cold, more so in hot alcohol, freely in ether, benzole, carbonic disulphide, and glacial acetic acid.

PARAIODBENZYLAMINES.

Alcoholic ammonia removed the bromine from the paraiodbenzylbromide with great ease: in fact, it was only necessary to warm the substances together in a flask to obtain a voluminous white precipitate consisting of the secondary and tertiary amines. If a more dilute solution was used, the tertiary amine alone was deposited; while a mixture of this and the secondary amine fell upon adding water. The liquid decanted from this precipitate was evaporated to dryness, and the residue separated by treatment with water into an insoluble bromide of the secondary and a soluble salt, probably the bromide of the primary amine, which, however, could not be obtained in quantity sufficient for examination.

It would seem that the primary amine can be formed in larger quantities under certain conditions, as, on one occasion, a basic oil which solidified after some time was obtained from the wash-waters, but this was unfortunately lost before it was examined, and all attempts to prepare a fresh portion were unsuccessful. The mixture of the secondary and tertiary amines, after thorough washing with water, was treated with hot alcohol, which separated without difficulty the more soluble secondary from the but slightly soluble tertiary amine.

Triparaiodbenzylamine, $(C_6H_4ICH_2)_3N$, was purified by recrystallization from ether, dried *in vacuo*, and analyzed.

I. 0.3609 gr. substance gave 8.08 cc. nitrogen, under a pressure of 745.6 mm. and a temperature of 20°.

II. 0.8461 gr. substance gave 21.08 cc. nitrogen, under 742.8 mm and 21°.

	Calculated for $(C_7H_6I)_3N$.	Found. I.	II.
Nitrogen	2.15	2.51	2.76

Properties. White needles, arranged in groups resembling hourglasses, with an agreeable odor; melting-point, 114½°; is turned gray by heating, and the melting-point is then much higher; insoluble in water and cold alcohol; very slightly soluble in boiling alcohol, easily in ether, benzole, and carbonic disulphide. A chloride could not be obtained by treating a solution of the base with hydrochloric acid.

Triparaiodbenzylamine chlorplatinate, $[(C_6H_4ICH_2)_3NH]_2PtCl_6$, appeared as a bulky yellow precipitate, on adding a solution of platinic chloride to the amine dissolved in ether. It was washed with alcohol, dried *in vacuo*, and analyzed: —

0.7812 gr. substance gave on ignition 0.0886 gr. platinum.

	Calculated for $[(C_7H_6I)_3NH]_2PtCl_6$.	Found.
Platinum	11.32	11.34

Yellow needles nearly insoluble in water and alcohol.

Diparaiodbenzylamine, $(C_6H_4ICH_2)_2NH$, was purified by repeated recrystallization from hot alcohol, dried *in vacuo*, and analyzed.

0.4050 gr. substance gave 12.33 cc. nitrogen, under a pressure of 763.8 mm. and a temperature of 25°.5.

	Calculated for $(C_7H_6I)_2NH$.	Found.
Nitrogen	3.12	3.40

Properties. White needles with square ends, having an odor somewhat resembling that of the nitrile; melting-point, 76°; insoluble in water; sparingly soluble in cold, freely in hot alcohol, and in ether, benzole, and disulphide of carbon.

The *chloride of the base*, obtained by adding hydrochloric acid to its alcoholic solution, crystallizes in thick, white plates, with a very high melting-point; nearly insoluble in water, slightly soluble in alcohol and benzole, freely in carbonic disulphide and glacial acetic acid. It was proved to be the chloride, by treating its nitric acid solution with argentic nitrate, when argentic chloride was precipitated.

The *bromide of the base* was formed under certain conditions during the preparation of the amines: it was purified by crystallization from alcohol. Short, thick, pointed, white prisms, with a pearly lustre, and a high melting-point; insoluble in water; somewhat soluble in alcohol, more so in ether, benzole, and carbonic disulphide; sparingly soluble in glacial acetic acid. It was proved to be the bromide of the diamine, by treating it with a solution of sodic hydrate, when a base was set free, melting after recrystallization from boiling alcohol at 76°; while bromine was detected in the sodic hydrate by the usual test with chlorine water and carbonic disulphide.

Diparaiodbenzylamine chlorplatinate, $[(C_6H_4ICH_2)_2NH_2]_2PtCl_6$, was obtained as a yellow precipitate on adding platinic chloride to an alcoholic solution of the base: it was washed with alcohol, dried *in vacuo*, and analyzed: —

0.3951 gr. substance gave on ignition 0.0609 gr. platinum.

	Calculated for $[(C_7H_6I)_2NH_2]_2PtCl_6$.	Found
Platinum	15.07	15.42

Properties. Pale yellow microscopic crystals, grouped like certain forms of frost, almost insoluble in water and alcohol.